

# Interplay between structure and density anomaly for an isotropic core-softened ramp-like potential

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## Abstract

Using molecular dynamics simulations and integral equations we investigate the structure, the thermodynamics and the dynamics of a system of particles interacting through a continuous core-softened ramp-like interparticle potential. We found density, dynamic and structural anomalies similar to that found in water. Analysis of the radial distribution function for several temperatures at fixed densities show a pattern that may be related to the origin of density anomaly.

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## I. INTRODUCTION

Water is an anomalous substance in many respects. Its specific volume at ambient pressure starts to increase when cooled below  $T = 4^{\circ}\text{C}$ . This density anomaly can be well explained by the tetrahedral structure of water. Each molecule forms hydrogen bonds with neighbors molecules by donating and receiving electrons from the hydrogens. But this is not the only peculiarity of water. While for most materials diffusivity decreases with increasing pressure, liquid water has an opposite behavior in a large region of the pressure-temperature phase diagram [1, 2, 3, 4, 5]. This diffusivity (or dynamic) anomaly is due to the following mechanism: the increase in pressure disturbs the tetrahedral structure of water by the inclusion of an interstitial fifth molecule that shares a hydrogen bond with another neighbor oxygen. As a result, the bond is weakened and the molecule is free to move. The shared bond breaks and the molecule, by means of a small rotation, connects to another molecule enabling the translational diffusion [3]. The structure and anomalies are therefore deeply related.

The quantification of structure usually employs Errington and Debenedetti's translational order parameter [1]  $t$ , that measures the tendency of pairs of molecules to adopt preferential separations, and Steinhardt's [6] orientational order parameter  $Q_6$ . For normal liquids,  $t$  and  $Q_6$  increase upon compression, because the system tends to be more structured. For systems with tetragonal symmetry [1] the suitable orientational order parameter is  $q$ , that quantifies the extent to which a molecule and its four nearest neighbors assume a tetrahedral arrangement. It was found that in SPC/E water both  $t$  and  $q$  decrease upon compression in a certain region of the pressure-temperature (P-T) phase diagram [1]. This region is referred as the region of structural anomalies.

Is the tetrahedral structure the only one where anomalies would exist? The answer to this question is no. Isotropic models are the simplest framework to understand the physics of liquid state anomalies. A number of such models, in which single component systems of particles interact via core-softened potentials [7] have been proposed. They possess a repulsive core that exhibits a region of softening where the slope changes dramatically. This region can be a shoulder or a ramp. These isotropic models are designed to represent interactions in water and other materials in an effective way.

Recently, we investigated a system of particles interacting through a core-softened, ramp-

like potential[8, 9] that has density, diffusion, and structural anomalies similar to that found for SPC/E water. In this work, we use the same model to investigate the relation between the local structure of the fluid, as measured by the pair distribution function, and the density anomaly.

## II. THE RESULTS

The model we study consists of a system of  $N$  particles of diameter  $\sigma$ , inside a cubic box whose volume is  $V$ , resulting in a density number  $\rho = N/V$ . The interacting effective potential between particles is given by

$$U^*(r) = 4 \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + a \exp \left[ -\frac{1}{c^2} \left( \frac{r - r_0}{\sigma} \right)^2 \right], \quad (1)$$

where  $U^*(r) = U(r)/\epsilon$ . The first term of Eq. (1) is a Lennard-Jones potential of well depth  $\epsilon$  and the second term is a Gaussian centered on radius  $r = r_0$  with height  $a$  and width  $c$ . With  $a = 5$ ,  $r_0/\sigma = 0.7$  and  $c = 1$ , this potential has two length scales within a repulsive ramp followed by a very small attractive well, as we can see in Figure 1.

The dimensionless pressure,  $P^*$ , temperature,  $T^*$ , and density,  $\rho^*$ , are given in units of  $\sigma^3/\epsilon$ ,  $k_B/\epsilon$ , and  $\sigma^3$ , respectively. Here  $k_B$  stands for the Boltzmann constant.

Using integral equation with the Rogers-Young Closure [10] it is possible to analyse quickly the entire phase diagram. For the model Eq. (1) was found density anomaly [8]. In the neighborhood of the density anomaly region, molecular dynamics simulations were carried out, in order to investigate density, diffusion, and structural anomalies. Besides the confirmation of the presence of density anomaly we demonstrated that diffusion and structural anomalies are also present in our model [8, 9].

The relation between the several anomalies presented for the potential Eq. (1) is shown in Fig. 7 of Ref. [9]. We found that the structural anomalous region have inside the diffusion anomaly region which in its turns englobes the density anomaly region. These hierarchy of anomalies is the same as the one found for the SPC/E water (compare Fig. 7 of reference [9] and Fig. 4 of Ref. [1]).

In order to understand the relation between structure and density anomaly, we analyse the pair distribution functions of our model (Fig. 2). We see clearly three well defined regimes, namely:

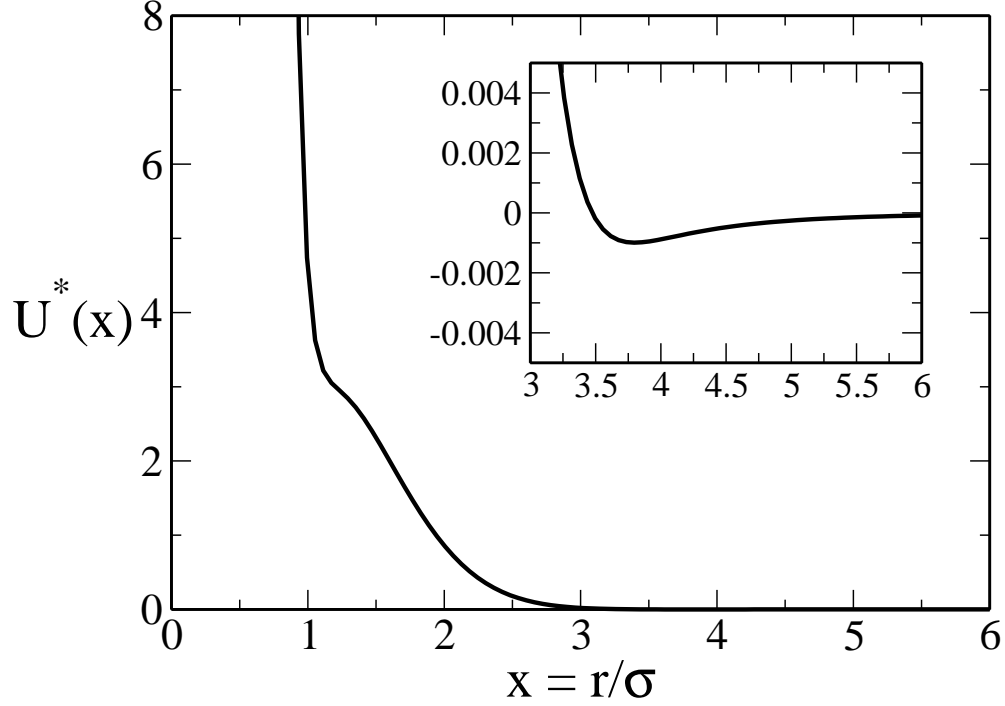


FIG. 1: Interaction potential from Eq. (1) with parameters  $a = 5$ ,  $r_0/\sigma = 0.7$ , and  $c = 1$ , in reduced units. The inset shows a zoom in the very small attractive part of the potential.

(i) For a low density, below the region where density anomaly occurs (see Fig. 3), the remarkable point is that the first peak (close to the core) of the  $g(r)$  are too modest, and the population of particles at this distance is negligible. Note the arrows indicating the direction of temperature increase.

(ii) For intermediate density, inside the region of density anomaly, we have a considerable increasing of the first peak of the  $g(r)$  compared to the low density regime, specially at low temperatures. Note that for temperatures  $T^* = 0.15, 0.18$ , and  $0.23$ , just inside the density anomaly domain (see the TMD line in Fig. 3) the  $g(r)$  had experience a special accented growth compared to the higher temperatures. In the first peak the bottom  $g(r)$  corresponds to the lowest temperature and the top, to the highest temperature. The second peak of the  $g(r)$ , close to  $2.5\sigma$ , has an opposite behaviour, and the arrow is downward.

(iii) For a high density, above the density anomaly region, the interesting thing to note is the inversion of the arrow in the first peak of  $g(r)$ . Close to the core, the lowest temperature has the highest first peak. The trend in the second peak remains unchanged.

This analysis suggests that the behaviour of the  $g(r)$  underlies the density anomaly effect

in a close way. The anomaly develops when the inner peak, close to core distances, becomes increasingly important. We see that the first peak of the  $g(r)$  tends to increase faster for low temperatures upon compression than for the high temperatures. This suggests a connection between density anomaly and structure depending on the derivative of the  $g(r \approx \sigma)$  with respect to the temperature at fixed density. A similar study of  $g(r)$  for several densities at constant temperature was also applied to show its pattern related to the structural anomaly region[9].

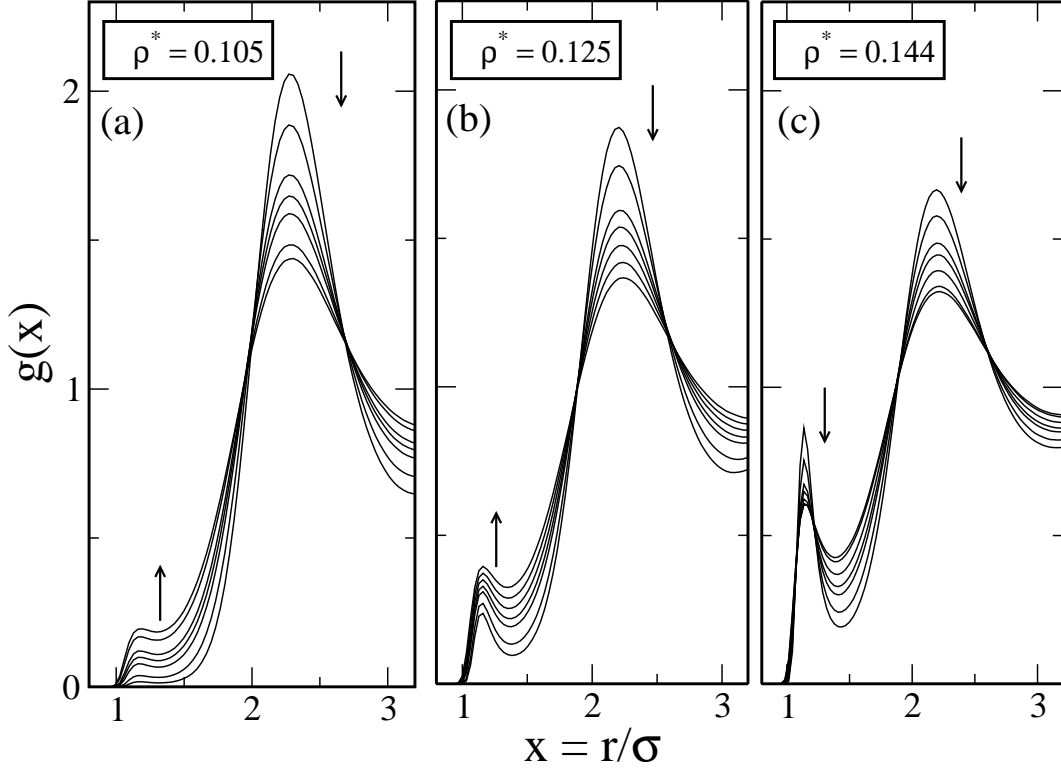


FIG. 2: Pair distribution functions for three densities and seven temperatures of our model Eq.(1). The densities are (a)  $\rho^* = 0.105$ , (b)  $\rho^* = 0.125$ , and (c)  $\rho^* = 0.144$ . These densities are the same as those illustrated in Fig. 3. The temperatures in (a), (b), and (c) are  $T^* = 0.15, 0.18, 0.23, 0.262, 0.3, 0.35$ , and  $0.4$ . The arrows indicate the direction of temperature growth, similar to the arrows in Fig. 3.

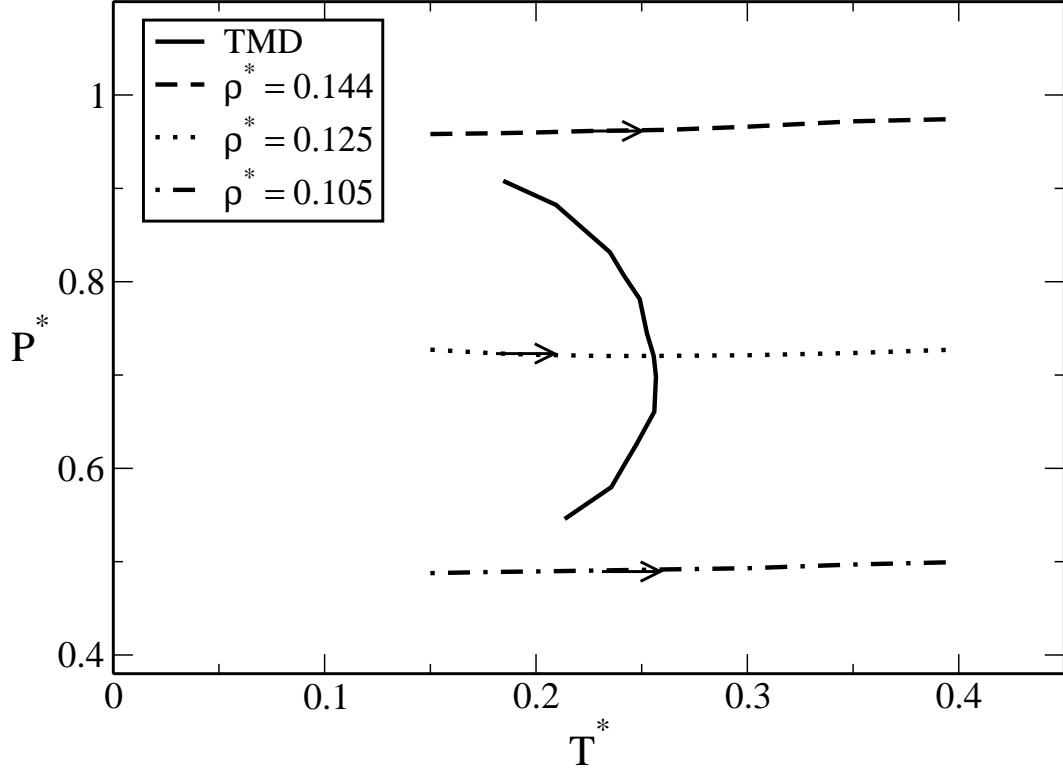


FIG. 3: Pressure-temperature phase diagram for the model Eq. (1). The three isochores shown in this figure correspond to the regions below, inside, and above the region where density anomaly occurs, i.e. inside the TMD line (solid line). The arrows indicate the temperature growth and help the analysis in Fig. 2.

### III. CONCLUSIONS

Using molecular dynamic simulations we have studied the density behavior, the diffusivity, and the structure of fluids interacting via a three-dimensional continuous core-softened potential with a continuous force. Our model exhibits a region of density anomaly, inside which the density increases as the system is heated at constant pressure, and a region of diffusion anomaly, where the diffusivity increases with increasing density [8]. In the pressure-temperature phase diagram, the density anomaly region lies inside the diffusion anomaly one. Complementary to the thermodynamic and dynamic anomalies, both  $t$  and  $Q_6$  behave anomalously in a large region of the temperature–density plane.

This continuous core-softened pair potential, despite not having long-ranged or directional interactions, exhibits thermodynamic, dynamic [8], and structural anomalies[9] similar to the

ones observed in SPC/E water [1, 2]. Therefore, the presence of anisotropy in the interaction potential is not a requirement for the presence of thermodynamic, dynamic and structural anomalies.

We also found that the pattern of isochoric change of the pair distribution function  $g(r)$  with temperature is closely related to the presence of density anomaly. The inset of this anomaly may be related to the derivative of population of molecules with respect to the temperature in a distance corresponding to the core distance.

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